HETA 88-377-2120 JUNE 1991 ARMCO COKE OVEN ASHLAND, KENTUCKY NIOSH INVESTIGATORS: Gregory M. Kinnes, M.S. Alan K. Fleeger, M.S. Sherry L. Baron, M.D.

I. <u>SUMMARY</u>

In July and December of 1989, the National Institute for Occupational Safety and Health (NIOSH) conducted environmental monitoring at a coke producing facility in Ashland, Kentucky, as part of the Health Hazard Evaluation Program. The focus of this sampling were the potential exposures to employees working in the by-products area.

Samples were collected from the ammonia concentrator, pump house, power house, exhauster building, and the sulfiban areas and included both general area samples and personal breathing zone samples from operators, helpers, welders, electricians, pipe fitters, repairmen, and other maintenance personnel. Contaminants that were sampled included ammonia, benzene, toluene, naphthalene, 1,1,1-trichloroethane, coal tar pitch volatiles (benzene soluble fraction), polynuclear aromatic hydrocarbons (PNAs), sulfates, phenol and cresol. In addition, colorimetric detector tube samples were collected for a variety of other potential contaminants.

The sampling results indicated overexposures to both benzene and coal tar pitch volatiles (CTPVs). Airborne levels of benzene ranged from non-detected (ND) to 117 parts per million (ppm). Three of the 17 benzene samples were above both the Occupational Safety and Health Administration (OSHA) Permissible Exposure Limit (PEL) of 1 ppm and the NIOSH Recommended Exposure Limit (REL) of 0.1 ppm. Airborne concentrations of CTPVs ranged from ND to 0.38 milligrams per cubic meter of air (mg/m³). Two of these six samples were above both the NIOSH REL of 0.1 mg/m³ and the OSHA PEL of 0.2 mg/m³. Several PNAs were detected including naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, and anthracene. Sample results for the other contaminants were below their relevant evaluation criteria.

The NIOSH investigators also examined the potential for conducting a epidemiological study to determine the cause-specific death rates among workers in the plant, by examining the personnel records. Given the small number of post-1981 workers and the short follow-up time period, an epidemiologic study was considered unlikely to yield meaningful information at this time.

The environmental sampling indicated that by-products area workers are potentially over-exposed to carcinogens, including benzene, CTPVs, and PNAs. The employees with the highest potential for exposure included the by-products pumphouse operator and maintenance workers. The extent of exposure was dependent on whether employees were performing repair tasks. Recommendations for reducing potential employee exposures are provided in this report.

KEYWORDS: SIC 3312 (Steel Works, Blast Furnaces (including Coke Ovens), and Rolling Mills) benzene, coal tar pitch volatiles, polynuclear aromatic hydrocarbons, ammonia, cancer, chemical recovery coke ovens, by-product coke ovens.

II. INTRODUCTION

On September 16, 1988, the National Institute for Occupational Safety and Health (NIOSH) received a request from the Oil, Chemical and Atomic Workers International Union (OCAW), Local 3-523, to investigate employee health concerns at the Armco, Inc. coke plant located in Ashland, Kentucky. The health concerns specified in this request included a variety of cancers of the kidney, colon, and lung, as well as lung disease.

NIOSH investigators visited the facility on December 12-13, 1988, and July 17-19 and December 11-12, 1989. During the visit on December 12th, 1988, an opening conference was held and attended by representatives from both OCAW and Armco. At this conference, representatives from the union expressed concerns that their members were developing cancers at a high rate, as well as concerns about exposures at the coke plant, particularly in the by-products area. Following this conference, NIOSH investigators toured the facility and reviewed records from the industrial hygiene program, the medical program, and employment and death records maintained by the corporation. Bulk samples were collected from the by-products area and informal interviews were held with employees and supervisors regarding occupational health concerns. A letter summarizing the initial findings and recommendations was distributed on January 17, 1989.

Due to the potential for exposure to several carcinogens, including benzene and polynuclear aromatic hydrocarbons (PNAs), further environmental sampling was deemed necessary. On July 17-19, 1989, NIOSH returned to conduct this sampling. General area and personal breathing-zone samples were collected throughout the by-products department. Individual compounds that were sampled for included: ammonia (NH₃), benzene, toluene, naphthalene, PNAs, sulfur dioxide (sulfates and sulfites), phenol, cresol, 1,1,1-trichloroethane, and the benzene soluble fraction of coal tar pitch volatiles (CTPVs). Colorimetric detector tube samples were also collected for various compounds (carbon monoxide, sulfur dioxide, nitrogen dioxide, carbon disulfide, phenol, xylene, hydrogen cyanide, hydrogen sulfide, pyridine, and olefin) throughout the by-products department.

The July 17-19, 1989, survey was concluded early due to inclement weather. Since many employee tasks occurred outdoors, the remaining sampling was postponed. NIOSH investigators returned on December 11-12, 1989, to complete the environmental sampling using the same protocol as in the previous survey.

III. BACKGROUND

Armco Steel, a major producer of iron and steel, purchased the coke operations located in Ashland, Kentucky, in December 1981. The annual capacity of this facility is approximately 1,000,000 tons of coke. Of the approximately 400 total employees who work at the coke oven, 55 work in the by-products area. Coal is used as one of the raw products in the making of coke which is used in the production of steel. Coke is a coherent, cellular, carbonaceous residue, remaining from the dry distillation of coking coal. In the coking process, the volatile components of the natural coals are driven off to form a substance with a substantially higher carbon content (approximately 94% in this case). By-product coke ovens are utilized at this facility for making coke and are designed and operated to permit the collection of the volatile materials evolved from the coking process. Epidemiological studies conducted in the 1960s and 1970s found elevated cancer rates among coke oven by-product area workers, but were unable to identify causative agents. (1.2)

The reactions during the carbonization of coal take place in three steps. Primary breakdown occurs at temperatures below 1296 degrees Fahrenheit (°F), yielding water, oxides of carbon, hydrogen sulfide, hydroaromatic compounds, paraffins, olefins, phenolic, and nitrogencontaining compounds. Secondary reactions occur in the stage above 1296°F, resulting in the evolution of large quantities of hydrogen and the formation of aromatic hydrocarbons and methane. During the final step, progressive removal of hydrogen from the residue in the oven produces the hard coke. During the carbonization process, about twenty to thirty percent by weight of the initial coal charge is evolved as mixed gases and vapors and is processed through the by-product department. Other substances in the raw gases and vapors leaving the ovens, which are liquids at ordinary temperatures, are NH₃ liquor, tar, and light oil. (3)

There are two operating batteries (a battery is a series of coke ovens) at the Armco facility which produce blast-furnace quality coke. A wet coal charge is approximately 28 tons and yields 20 tons of furnace coke per push (a push consists of filling the coke oven with coal, and then completing the coking cycle). On the average, they have 30-33 pushes per battery per shift. The by-product area at this facility is comprised of the NH₃ concentrator, pump house, power house, exhauster building, and the sulfiban. Job classifications in the by-products area include maintenance, electrician, welder, pipe fitter, repairman, and operators/helpers.

IV. EVALUATION DESIGN AND METHODS

A. INDUSTRIAL HYGIENE

During the initial survey, bulk samples were collected of the coal tar sludge and light oil for qualitative identification of individual compounds. The samples were submitted for total hydrocarbon and individual PNA analysis. The samples were extracted with benzene and analyzed via gas chromatography according to NIOSH Methods 5515 and 1500 with slight modifications.⁽⁴⁾

Based on the information collected during the initial survey and the results from the bulk analysis, air samples were collected throughout the by-products department to both identify and quantitate airborne levels of a variety of different compounds. The air samples were collected in two visits to the facility. The by-products pumphouse, exhauster building, ammonia concentrate, sulfiban, and power house were the primary locations where area samples were collected for the qualitative identification of airborne compounds. In addition, personal breathing-zone air samples were collected on employees in each of the aforementioned areas and on maintenance workers for quantitative purposes. Individual compounds sampled for included ammonia, benzene, toluene, naphthalene, PNAs, sulfite, sulfate, 1,1,1-trichloroethane, phenol, cresol, and total benzene solubles. In addition, instantaneous detector tube samples were collected throughout the by-products department for ammonia, carbon disulfide, carbon monoxide, hydrogen cyanide, hydrogen sulfide, nitrogen dioxide, sulfuric acid, sulfur dioxide, olefins, pyridine, and several volatile organic compounds.

Air samples for ammonia were collected by drawing air at a rate of 0.05 liters per minute (lpm) through a sulfuric acid-treated silica gel tube connected via Tygon® tubing to a battery powered pump. The samples were prepared for analysis by desorbing with hydrochloric acid and heating in a warm water bath. An aliquot of each sample was analyzed for ammonium ion concentrations by ion chromatography according to NIOSH Method S347.⁽⁴⁾

Air samples for volatile organic compounds (benzene, toluene, naphthalene, and 1,1,1-trichloroethane) were collected by drawing air at a rate of 0.05 lpm through a standard charcoal tube connected via Tygon® tubing to a battery powered pump. A select number of area samples were first submitted for qualitative identification by gas chromatograph-mass spectrometer (GC-MS) analysis. The remaining charcoal tubes were then quantitated via GC-MS according to NIOSH Method 1501⁽⁴⁾ based on the compounds identified during the qualitative analysis.

Air samples for PNAs were collected by drawing air at a rate of 1.0 lpm, first, through a 37 millimeter Zefluor® filter, and then, through an ORBO 42 sorbent tube, connected via Tygon® tubing to a battery powered pump. The filters and tubes were extracted with benzene and analyzed by gas chromatography according to NIOSH Method 5515.⁽⁴⁾

Air samples for sulfur dioxide (sulfite/sulfate ions) were collected by drawing air at a rate of 1.0 lpm through a cellulose filter and potassium hydroxide treated pad connected in series, via Tygon® tubing, to a battery powered pump. The filters were analyzed by ion chromatography according to NIOSH Method 6004.⁽⁴⁾

Air samples collected for phenol and cresol were collected by drawing air at a rate of 0.04 lpm through a XAD-7 sorbent tube connected via Tygon® tubing to a battery powered pump. The samples were desorbed in methanol and analyzed by high performance liquid chromatography by the Occupational Safety and Health Administration's (OSHA) Method 32.⁽⁵⁾

B. MEDICAL

The union's primary request to NIOSH was to determine if there is an increased rate of cancer among the workers in the coke plant, particularly in the by-products area. Studies conducted elsewhere during the 1970's on a large group of coke oven workers found elevated rates of digestive tract cancers in the by-products departments but could not identify the causative agents.^(1,2) In order to determine if the Armco plant also has elevated rates of cancer an epidemiological investigation which determined the cause-specific death rates among workers in the plant would be necessary.

V. <u>EVALUATION CRITERIA</u>

As a guide to the evaluation of the hazards posed by workplace exposures, NIOSH field staff employ environmental evaluation criteria for the assessment of a number of chemical and physical agents. These criteria are intended to suggest levels of exposure to which most workers may be exposed up to 10 hours per day, 40 hours per week for a working lifetime without experiencing adverse health effects. It is, however, important to note that not all workers will be protected from adverse health effects even though their exposures are maintained below these levels. A small percentage may experience adverse health effects because of individual susceptibility, a pre-existing medical condition, and/or a hypersensitivity (allergy). In addition, some hazardous substances may act in combination with other workplace exposures, the general environment, or with medications or personal habits of the worker to produce health effects even if the occupational exposures are controlled at the level set by the criterion. These combined effects are often not considered in the evaluation criteria.

Also, some substances are absorbed by direct contact with the skin and mucous membranes, and thus potentially increase the overall exposure. Finally, evaluation criteria may change over the years as new information on the toxic effects of an agent become available.

The primary sources of environmental evaluation criteria for the workplace are the following:

1) NIOSH Recommended Exposure Limits (RELs)⁽⁶⁾, 2) the American Conference of
Governmental Industrial Hygienists' (ACGIH) Threshold Limit Values (TLVs)⁽⁷⁾, and 3) the
U.S. Department of Labor, Occupational Safety and Health Administration (OSHA)
Permissible Exposure Limits (PELs)⁽⁸⁾. The OSHA PELs may be required to take into
account the feasibility of controlling exposures in various industries where the agents are used;
the NIOSH RELs, by contrast, are based primarily on concerns relating to the prevention of
occupational disease. In evaluating the exposure levels and the recommendations for reducing
these levels found in this report, it should be noted that the lowest exposure criteria was used;
however, industry is legally required to meet those levels specified by the OSHA standard.

A time-weighted average (TWA) exposure refers to the average airborne concentration of a substance during a normal 8 to 10-hour workday. Some substances have recommended short-term exposure limits (STELs) or ceiling values which are intended to supplement the TWA where there are recognized toxic effects from high short-term exposures.

A. BENZENE

Benzene is a colorless, highly flammable, non-polar liquid, with an odor characteristic of aromatic hydrocarbons. Acute exposure causes central nervous system depression. Headache, dizziness, nausea, convulsions, coma, and death may result. Chronic exposure to benzene is well documented to cause blood changes, results in depression of the hematopoietic system, and is associated with an increased incidence of leukemia. The most significant toxic effect of benzene exposure is an insidious and often irreversible injury to the bone marrow. Long-term exposures to low concentrations have been observed to have an initial stimulant effect on the bone marrow, followed by aplasia and fatty degeneration. (9,10,11) Both NIOSH and the International Agency for Research on Cancer (IARC) have concluded that recent epidemiologic studies have established the relationship between benzene exposure and the development of acute myelogenous leukemia and that there is sufficient evidence to conclude that benzene is carcinogenic to humans. (12,13)

NIOSH recommends that occupational exposures to benzene be controlled so that employees are not exposed to concentrations greater than 0.1 parts per million (ppm), determined as a TWA concentration for up to a 10-hour work shift in a 40-hour work week. NIOSH further recommends a 15 minute STEL of 1.0 ppm. Although NIOSH has established these guidelines which should not be exceeded, the Institute still urges

that exposures be reduced to the lowest feasible level because it is not at present possible to establish thresholds for carcinogens which will protect 100% of the population. The ACGIH currently has a TLV of 10 ppm and has listed benzene as a suspected human carcinogen. However, the ACGIH has included benzene on its 1990-1991 Notice of Intended Changes which will establish a lower TLV of 0.1 ppm and recognizes benzene as a confirmed human carcinogen. The ACGIH has not established a STEL for benzene. OSHA has established a PEL for benzene at 1.0 ppm, as an 8-hour TWA. OSHA has also established a 15-minute exposure limit of 5.0 ppm.

B. COAL TAR PITCH VOLATILES - POLYNUCLEAR AROMATIC HYDROCARBONS

Polynuclear aromatic compounds (PNAs) are chemical species that consist of two or more fused aromatic rings. They are often associated with the combustion or pyrolysis of organic matter, especially coal, wood, and petroleum products. Materials associated with these processes have been demonstrated to contain compounds that have been shown to cause cancer in laboratory animals and, in some cases, humans. There are few dose-related relationships for the PNA mixtures that may be found in these processes, and no "safe" exposures to PNA aerosols. Although the application of laboratory animal data for PNA compounds to estimate human risk is very difficult, any occupational exposure to potentially carcinogenic matter is a cause for concern and exposures should be reduced to the lowest feasible level.

NIOSH recommends that occupational exposures to coal tar be controlled so that employees are not exposed to coal tar, coal tar pitch, creosote, or mixtures of these substances at a concentration greater than 0.1 milligrams per cubic meter (mg/m³) of the benzene- (or cyclohexane-) extractable fraction of the sample, determined as a TWA concentration for up to a 10-hour work shift in a 40-hour work week. Both ACGIH and OSHA set their standards at 0.2 mg/m³ for a normal 8-hour workday or 40-hour workweek. Individual PNA measurements serve to establish the presence of coal tar pitch volatiles (CTPVs) and indicate the presence of known or suspected carcinogens or other genotoxic compounds in the workplace, which would dictate additional control measures.

The potential adverse health effects of PNAs are well recognized. Several PNAs, such as benzo(a)anthracene and pyrene, have been shown to be carcinogenic in animals. Excess risk of lung cancer, oral cancer, and skin neoplasms (benign and malignant) have been found in working populations handling coal tar products which NIOSH has defined to include coal tar, coal tar

pitch, and creosote. A TWA exposure of 0.2 microgram per cubic meter (ug/m³) was recommended by the coke oven advisory committee for benzo(a)pyrene under the OSHA 29 CFR 1910.1029 coke oven emissions standard, but was not adopted. A special NIOSH hazard review of chrysene recommended that it be controlled as an occupational carcinogen. Also, ACGIH includes chrysene and benzo(a)pyrene in its list of industrial substances suspected of having carcinogenic potential in man. The carcinogenic potential of other PNAs (benzo(a)anthracene, anthracene, pyrene, and fluoranthene) has also been documented.⁽¹⁵⁾

VI. RESULTS and DISCUSSION

A. INDUSTRIAL HYGIENE

Personal breathing zone and area air sampling results for volatile organic compounds are shown in Table I. Benzene was the major airborne contaminant identified. Toluene, naphthalene, and 1,1,1-trichloroethane were also identified in lower concentrations. The benzene concentrations ranged from non-detected (ND) to 117.0 ppm. Three of the 17 samples for benzene (1, 1.9, 117 ppm) were above both the OSHA PEL of 1 ppm and the NIOSH REL of 0.1 ppm. Eight other samples had benzene concentrations which ranged from 0.49-0.95 ppm, all above the NIOSH REL. Benzene was either not detected or found only in trace quantities on the remaining six samples.

These 17 samples for benzene were collected during two surveys: ten samples in July, 1989, and seven in December, 1989. The air samples collected in July ranged from ND to 0.83 ppm while the December samples detected higher concentrations, ranging from 0.49 to 117 ppm. The three samples that had benzene concentrations above both the OSHA PEL and NIOSH REL were collected in December from the by-products pumphouse operator (117 ppm), from an area in the by-products pumphouse (1.9 ppm), and on a maintenance worker in the exhauster building (1.0 ppm). Both the byproducts pumphouse operator and the maintenance worker were performing repairs during the time the samples were collected. The samples which indicated airborne concentrations of benzene above the NIOSH REL were collected from maintenance workers in the exhauster building and by-products pumphouse, a foreman in the exhauster building and an area located in the by-products pumphouse. The remaining contaminants that were identified were all present in concentrations below their relevant evaluation criteria. Toluene concentrations ranged from ND to 12.0 ppm. Naphthalene concentrations ranged from ND to 3.6 ppm. Finally, 1,1,1trichloroethane concentrations ranged from ND to a trace amount.

Personal breathing zone and area air sampling results for CTPVs (benzene soluble fraction) are shown in Table II. Six samples were collected with concentrations ranging from ND to 0.38 mg/m³. Two of these six samples (0.23 and 0.38 mg/m³) were above both the NIOSH REL of 0.1 mg/m³ and the OSHA PEL of 0.2 mg/m³. A sample collected from the same by-products pumphouse operator mentioned above had a concentration of 0.38 mg/m³, while a sample from an exhauster building maintenance worker had a concentration of 0.23 mg/m³.

The environmental background information for the PNA samples collected during the evaluation are included in Table III. This table includes sample number, type of sample (personal breathing zone or area), air volume (in liters), and sample location. Individual PNA results for these samples are shown in Table IV. Several PNAs were detected, including naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, and anthracene.

Personal breathing zone and area sampling results for ammonia are located in Table V. Ammonia concentrations ranged from ND to 6.5 ppm. These concentrations are well below the NIOSH REL and ACGIH TLV for ammonia of 25 ppm. The other contaminants that were included in the environmental sampling were either not detected or present only in trace concentrations.

None of the Armco employees surveyed were wearing respirators at the time these samples were collected. Employees were wearing protective gloves and did use limited forms of other personal protective equipment (such as disposable coveralls, etc.). In addition, liquid spills and leaking valves and pumps were observed in most of the byproduct departments, which resulted in large quantities of by-product liquids trapped in the diked containment areas. This was especially the case in the by-product pumphouse.

B. MEDICAL

The NIOSH investigators examined the potential for conducting an epidemiological study by examining the personnel records. Since the plant was purchased by Armco in December 1981, there were no records of anyone who was not currently employed at the time of purchase. Phone conversations with the previous owner found that there were not complete employment records on all workers prior to 1981. Given the small number of post-1981 workers and the short follow-up time period, an epidemiologic study is unlikely to yield meaningful information at this time. It would however, be possible to put together information on the post-1981 workforce including their exposure information, which could then be evaluated at a future time (5-10 years).

Therefore, because of the limitations of such a study, NIOSH agreed, with the understanding of the union, to conduct such a mortality study if the company would provide the clerical support to identify and code the information on the workers. Although, the company initially agreed to provide this service, they were unable to complete the work because of financial constraints.

VII. CONCLUSIONS

The environmental air sampling indicated that workers in the by-products area are potentially exposed to high levels of carcinogens, including benzene, CTPVs, and PNAs. The employees with the highest potential for exposure include the by-products pumphouse operator and maintenance workers. These employees were exposed to airborne concentrations of benzene and CTPVs above both NIOSH and OSHA criteria. These exposures seem to be dependant on the work tasks being performed. During this investigation, these employees were performing pump and exhauster repairs. Also, general area air samples collected from the by-products pumphouse and the exhauster building indicated high concentrations of benzene.

VIII. RECOMMENDATIONS

Preliminary recommendations made after the initial site visit were included in a letter, dated January 17, 1989, which was sent to the company and union. Additional recommendations are made based on the environmental sampling results and observations. All of these recommendations, presented below, will help to further reduce potential employee exposures.

- 1. An environmental sampling program which includes maintenance activities should be developed to determine the extent of exposures and proper control measures that should be implemented. Engineering and administrative controls should be implemented where they are feasible. Respirators should only be used where engineering and administrative controls would not effectively reduce the potential for employee exposures. If respirators are deemed necessary, a program for proper selection, use, and maintenance should be developed which meets the requirements of OSHA regulations (29 CFR Parts 1910.134, 1910.1028, and 1910.1029).
- A preventative maintenance program should be developed to reduce the need for major repairs where the highest probability for exposures exists. This preventative maintenance program should also be evaluated by environmental sampling to determine proper controls for limiting exposures.

- 3. The general housekeeping procedures should be improved, including the immediate cleanup and repair of leaks. A spill cleanup procedure should be implemented throughout the by-products area to immediately respond to any liquid spills that may occur. In addition, the diking containments should be drained and cleaned of any residual spills that may occur.
- 4. Where it is feasible, operators' booths in the by-products buildings should be moved outside to isolate the operators from the sources of exposure. All operators' booths should have a supply of outside, filtered air to reduce the potential for exposure to airborne contaminants. The operator booths should also be kept under positive pressure.

IX. <u>REFERENCES</u>

- 1. Redmond CK, Strobino BR, Cypess RH [1976]. Cancer experience among coke by-product workers. Ann NY Acad Sci *271*:102-115.
- NIOSH [1973]. Criteria for a recommended standard: occupational exposure to coke oven emissions. Cincinnati, Ohio: U.S. Department of Health, Education, and Welfare, Health Services and Mental Health Administration, National Institute for Occupational Safety and Health; DHEW (NIOSH) Publication No. 73-11016.
- 3. United States Steel [1957]. The making, shaping and treating of steel. 7th ed. Pittsburgh, PA: United States Steel Corporation, pp. 90-138.
- 4. Eller RM, ed. [1989]. NIOSH manual of analytical methods. 3rd rev. ed. Cincinnati, Ohio: U.S. Department of Health and Human Services, Public Health Service, Centers for Disease Control, National Institute for Occupational Safety and Health, DHHS (NIOSH) Publication No. 84-100.
- 5. OSHA [1987]. Chemical information manual. Washington, DC: U.S. Department of Labor, Occupational Safety and Health Administration, OSHA instruction CPL 2-2.43.
- 6. CDC [1988]. NIOSH recommendations for occupational safety and health standards 1988. Atlanta, GA: U.S. Department of Health and Human Services, Public Health Service, Centers for Disease Control; National Institute for Occupational Safety and Health. MMWR 37 (suppl S-7).
- 7. ACGIH [1990]. Threshold limit values and biological exposure indices for 1990-91. Cincinnati, Ohio: American Conference of Governmental Industrial Hygienists.

- 8. Code of Federal Regulations [1989]. OSHA Table Z-1. 29 CFR 1910.1000. Washington, DC: U.S. Government Printing Office, Federal Register.
- ACGIH [1986]. Documentation of the threshold limit values and biological exposure indices. 5th ed. Cincinnati, Ohio: American Conference of Governmental Industrial Hygienists.
- 10. Proctor NH, Hughes JP, Fischman ML [1988]. Chemical hazards of the workplace. 2nd ed. Philadelphia, PA: J.B. Lippencott Company, pp. 90-93.
- 11. NIOSH [1977]. Occupational diseases a guide to their recognition. rev. ed. Cincinnati, Ohio: U.S. Department of Health, Education, and Welfare, Public Health Service, Centers for Disease Control, National Institute for Occupational Safety and Health, DHEW (NIOSH) Publication No. 77-181.
- IARC [1982]. IARC monographs on the evaluation of the carcinogenic risk of chemicals to humans: some industrial chemicals and dye-stuffs. Vol. 29. Lyon, France: World Health Organization, International Agency for Research on Cancer, pp. 93-148.
- 13. NIOSH [1986]. NIOSH testimony the Occupational Safety and Health Administration's proposed rule on occupational exposure to benzene, March 20, 1986, OSHA Docket No. 11-059C. Cincinnati, Ohio: U.S. Department of Health and Human Services, Public Health Service, Centers for Disease Control, National Institute for Occupational Safety and Health.
- 14. Braunwald E, Isselbacher KJ, Petersdorf RG, Wilson JD, Martin JB, Fauci AS, eds. [1987]. Harrison's principles of internal medicine. 11th ed. New York, NY: McGraw-Hill Book Company, pp. 254-262.
- 15. NIOSH [1978]. Criteria for a recommended standard: occupational exposure to coal-tar products. Cincinnati, Ohio: U.S. Department of Health, Education, and Welfare, Health Services and Mental Health Administration, National Institute for Occupational Safety and Health; DHEW (NIOSH) Publication No. 78-107.
- 16. NIOSH [1976]. Health hazard evaluation report: Western Roofing Co., Sellers and Marquis Roofing Co., A.J. Shirk Co., and Quality Roofing Co., Kansas City, MO. Cincinnati, OH: U.S. Department of Health, Education, and Welfare, Public Health Service, Centers for Disease Control, National Institute for Occupational Safety and Health, NIOSH Report No. HHE 75-194-324, NTIS No. PB-269-112/A03.

 NIOSH [1981]. Hazard evaluation and technical assistance report: Mid-South Terminals, Memphis, TN. Cincinnati, OH: U.S. Department of Health and Human Services, Public Health Service, Centers for Disease Control, National Institute for Occupational Safety and Health, NIOSH Report No. HETA 80-206-1164, NTIS No. PB-84-149-178/A03.

X. <u>AUTHORSHIP AND ACKNOWLEDGEMENTS</u>

Report Prepared by: Gregory M. Kinnes, M.S.

Industrial Hygienist

Industrial Hygiene Section

Sherry L. Baron, M.D.

Medical Officer Medical Section

Field Assistance: Alan K. Fleeger, M.S.

Industrial Hygienist

Larry DeArmond

Industrial Hygiene Technician Industrial Hygiene Section

Originating Office: Hazard Evaluations and Technical

Assistance Branch

Division of Surveillance, Hazard Evaluations and Field Studies

Report Typed by: Gregory M. Kinnes

Kathleen Conway

XI. <u>DISTRIBUTION AND AVAILABILITY OF REPORT</u>

Copies of this report may be freely reproduced and are not copyrighted. Single copies of this report will be available for a period of 90 days from the date of this report from the NIOSH Publications Office, 4676 Columbia Parkway, Cincinnati, Ohio 45226. To expedite your request, include a self-addressed mailing label along with your written request. After this time, copies may be purchased from the National Technical Information Service (NTIS), 5285 Port Royal, Springfield, Virginia 22161. Information regarding the NTIS stock number may be obtained from the NIOSH Publications Office at the Cincinnati address. Copies of this report have been sent to:

- 1. Armco Steel, Ashland, Kentucky
- 2. OCAW International
- 3. OCAW Local 3-523
- 4. NIOSH, Atlanta Regional Office
- 5. Department of Labor\OSHA Region IV

For the purpose of informing affected employees, copies of this report shall be posted by the employer in a prominent place accessible to the employees for a period of 30 calendar days.

Page 16 - Health Hazard Evaluation Report No. 88-377

TABLE I
Personal and Area Air Samples for Volatile Organic Compounds
ARMCO COKE OVEN, Ashland, Kentucky / HETA 88-377 / July/December 1989

					Concentrati	ion (PPM)	
Sample #	Date	Location	Duration (Minutes)	Benzene	Toluene	Naphthalene	1,1,1,-Trichloro ethane
35	7/19	Exh Maint	401	0.63	T	ND	T
31	7/19	Sampleman	261	ND	ND	ND	ND
41	7/19	Maint BP/Exh	395	0.78	T	ND	ND
43	7/19	Exh Maint	376	0.83	T	ND	ND
47	7/19	Sulfiban Maint	367	ND	ND	ND	ND
50	7/19	Maint BP/NH ₃	384	0.65	T	ND	ND
64	7/19	Exh Operator	495	T	ND	ND	ND
65	7/19	BP Operator	451	T	ND	ND	ND
66	7/19	BP Foreman	408	T	ND	ND	ND
67	7/19	Powerhouse Foreman	394	ND	ND	ND	ND
120	12/12	Exh Maint	398	0.95	ND	ND	NA
121	12/12	Exh Maint	368	0.49	ND	ND	NA
122	12/12	Exh Foreman	398	0.57	ND	ND	NA
123	12/12	Exh Maint	392	1.00	T	ND	NA
125	12/12	BP Area Sample	408	0.69	ND	0.66	NA
127	12/12	BP Operator	398	117	12.5	3.65	NA
128	12/12	Exh Area Sample	396	1.9	T	ND	NA
Evaluation C				Co			
	NIOSH OSHA			0.1,1 ^{Ca} 1,5	100,150 100,150	10,15 10,15	350 350,450
	ACGIH			1,5 10 ^b	100,150	10,15	350,450
				-	,	- , -	,

a = In most instances the evaluation criteria shown list the time-weighted average exposure limit first, followed by the short-term (ceiling) exposure limit (when appropriate).

Ca = Potential occupational carcinogen.

b = ACGIH has proposed to reduce their exposure limit for benzene, a human carcinogen, to $0.1~\mathrm{ppm}$.

T=Trace Value (analytical Results Between LOD & LOQ)

 $[\]begin{array}{ll} ND = Nondetectable & BP = By\text{-Products Pumphouse} \\ NA = Not \ Analyzed & NH_3 = Ammonia \ concentrate \\ Exh = Exhauster \ Building & Maint = Maintenance \ Worker \end{array}$

TABLE II

Personal and Area Air Samples for Total Benzene Soluble Fraction ARMCO COKE OVEN Ashland, Kentucky HETA 88-377 December 12, 1989

Sample #	Location	Duration (min)	Concentration (mg/m³)		
103	Exhauster Maintenance	268	0.03		
105	Exhauster Maintenance	243	ND		
109	Maintenance Foreman	388	0.08		
111	Exhauster Maintenance	362	0.23		
115	Area Sample By-Products	381	0.03		
117	By-Products Operator	384	0.38		

TABLE III

Environmental PNA Background Information ARMCO COKE OVEN Ashland, Kentucky HETA 88-377 July/December 1989

Sample # (Filter/Tube)	Туре	Sample Duration (minutes)	Location
2/3	Area	419	NH ₃ Concentrate 6th Floor
6/7	Area	442	BP Pumphouse
12/13	Area	433	Exhauster Bldg
16/17	Area	409	Sulfiban
29/30	BZ	262	Sampleman
33/34	BZ	403	Exhauster Maintenance
36/37	BZ	379	BP Pumphouse Maintenance
39/40	BZ	395	BP Pumphouse Maintenance
55/56	Area	373	Battery #3 Charge Car
57/58	Area	370	Battery #4 Charge Car
61/62	BZ	196	BP Pumphouse Operator
68/69	BZ	408	BP Pumphouse Foreman
102/103	BZ	268	Exhauster Maintenance
104/105	BZ	243	Exhauster Maintenance
108/109	BZ	388	Exhauster Maintenance
110/111	BZ	362	Exhauster Maintenance
114/115	Area	381	BP Pumphouse
116/117	BZ	384	BP Pumphouse Operator

BZ = Breathing Zone $NH_3 = Ammonia$

TABLE IV

Personal and Area Air Samples for PNA's ARMCO COKE OVEN Ashland, Kentucky HETA 88-377 July/December 1989

Concentration in ug/m³

i 											0								
	Sample Number	2* 3**	6 7	12 13	16 17	29 30	33 34	36 37	39 40	55 56	57 58	61 62	68 69	102 103	104 105	108 109	110 111	114 115	116 117
Napht	thalene	130	2700	1200	100	60	600	770	730	180	650	610	230	173	123	103	124	2698	5145
Acena	aphthylene	Т	410	60	Т	Т	20	20	20	30	30	60	10	4	Т	3	3	147	313
Acena	aphthene	ND	3	Т	ND	ND	Т	ND	ND	5	Т	ND	ND	100	ND	ND	ND	5	10
Fluore	•	ND	180	10	ND	ND	5	Т	4	17	10	10	Т	Т	ND	Т	Т	24	47
	anthrene	Т	110	20	Т	ND	6	4	5	50	30	20	Т	Т	ND	Т	Т	22	32
	racene	ND	20	T	ND	ND	Т	ND	ND	10	10	T	ND	ND	ND	ND	ND	5	7
Fluora	anthene	ND	170	T	ND	ND	ND	ND	ND	30	30	T	ND	ND	ND	ND	ND	Т	ND
Pyrer	ne	ND	10	Т	ND	ND	ND	ND	ND	20	30	ND	ND	ND	ND	ND	ND	Т	ND
Benz((a)anthracene	ND	ND	ND	ND	ND	ND	ND	ND	10	10	ND	ND	ND	ND	ND	ND	ND	ND
Chrys	sene	ND	ND	ND	ND	ND	ND	ND	ND	10	10	ND	ND	ND	ND	ND	ND	ND	ND
Benzo	o(b)Fluoranth.	ND	ND	ND	ND	ND	ND	ND	ND	10	20	ND	ND	ND	ND	ND	ND	ND	ND
Benzo	o(k)Fluoranth.	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	o(e)Pyrene	ND	ND	ND	ND	ND	ND	ND	ND	5	10	ND	ND	ND	ND	ND	ND	ND	ND
	o(a)Pyrene	ND	ND	ND	ND	ND	ND	ND	ND	8	10	ND	ND	ND	ND	ND	ND	ND	ND
		ND	ND	ND	ND	ND	ND	ND	ND	T	10	ND	ND	ND	ND	ND	ND	ND	ND
	10(1,2,3-cd)Pyr.																		
	nz(a,h)anthrac.	ND	ND	ND	ND	ND	ND	ND	ND	T	T	ND	ND	ND	ND	ND	ND	ND	ND
Benz((g,h,i)Peryl.	ND	ND	ND	ND	ND	ND	ND	ND	T	10	ND	ND	ND	ND	ND	ND	ND	ND

^{* -} Sample Filter
** - Sample Tube
T - Trace Value (Analytical Results between LOD & LOQ)

ND - Non detectable

Page 20 - Health Hazard Evaluation Report No. 88-377

TABLE V

Personal and Area Air Samples For Ammonia ARMCO COKE OVEN Ashland, Kentucky HETA 88-377 July 18-19, 1989

SAMPLE#	ТҮРЕ	LOCATION	MINUTES	VOLUME (liters)	Concentration (PPM)
1	GA	Exhauster Bldg	434	2	1.4
4	GA	By-Prod Pumphouse	416	21	6.5
5	GA	Sulfiban	416	21	0.9
8	GA	NH ₃ Concentrate	396	20	0.9
28	GA	Sample Room	272	14	Т
46	BZ	Sulfiban Operator	368	18	Т
49	BZ	NH ₃ Concentrate Maintenance	388	19	1.0
53	BZ	NH ₃ Concentrate Maintenance	386	19	Т

T = Trace Value (Analytical Result Between LOD & LOQ)

GA = General area air sample

BZ = Breathing zone air sample

NH₃= Ammonia